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Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

Influence of Promotor, H_2O and H_2S on the Hydrodeoxygenation of Biomass Pyrolysis Vapor over MoS_2 Catalysts

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Catalytic hydropyrolysis combines fast pyrolysis with catalytic upgrading by hydrodeoxygenation (HDO) in a single step for the production of fuel oil from biomass in which reactive pyrolysis vapors are upgraded before condensation. Catalyst activity and lifetime is challenged by carbon deposition and by the presence of alkali, nitrogen, sulfur and water. In this contribution, a combined experimental, characterization (in-situ Extended X-Ray Absorption Fine Structure, EXAFS) and theoretical (Density Functional Theory, DFT) study of catalytic HDO of biomass model compounds over MoS_2 based catalysts is presented with emphasis on the influence of water and H_2S.

1. Scope

The aim of this work is to study the influence of promotion and H_2O/H_2S on catalytic HDO of biomass model compounds and their mixtures over MoS_2 catalysts through a combined experimental and theoretical investigation. $MoS_2/MgAl_2O_4$ and Co(/Ni)-$MoS_2/MgAl_2O_4$ catalysts with 3.3 wt% Mo and Co(/Ni):Mo molar ratio = 0.3 have been prepared by incipient wetness impregnation and sulfidation with 10-12% H_2S/H_2 at 360-400°C. Ethylene glycol (EG) is a simple model polyol representing the cellulosic fraction of biomass. Catalytic HDO tests were conducted in a fixed bed reactor at 350-450°C, 28 bar H_2 and 545-2200 ppm H_2S (m_{cat} = 0.5-4 g, $feed_{EG}$ = 0.14 mL/min, EG Weight Hourly Space Velocity (WHSV) = 2.3-19 h^{-1}, 40 barg, balance N_2). Products were separated into gas (online analysis by GC-TCD) and liquid (offline analysis by GC-MS/FID). DFT calculations were used to predict the influence of varying H_2O/H_2S ratios on the stability of the sulfide/oxide phases and reaction pathways. The Quantum Espresso code[1] was applied in combination with the BEEF-vdW exchange correlation functional[2]. In-situ Quick-EXAFS was conducted at the Swiss Light Source (SLS) SuperXAS beamline[3] at the Co-, Ni- and Mo- K-edge of prepared catalysts during sulfidation and subsequent exposure to varying H_2O/H_2S ratios at 400-450°C using an appropriate in-situ cell[4]. Catalysts and support material have also been analyzed using other techniques such as Transmission Electron Microscopy (TEM), ICP-OES, NH_3-TPD, XRD, BET and Raman spectroscopy.

2. Results and discussion

Co(/Ni)-$MoS_2/MgAl_2O_4$ catalysts were active and moderately selective for EG HDO. 100% conversion was obtained for 50 h on stream at 400°C with 545 ppm H_2S and EG WHSV = 2.3 h^{-1}. At these conditions, a moderate HDO product yield (ethane and ethylene) of 40-45% was observed together with an undesired cracking (C_1: CO, CO_2, CH_4) yield of 30-35%. EG conversion over un-promoted $MoS_2/MgAl_2O_4$ (WHSV = 6.2 h^{-1}) showed a conversion >80% and an initial HDO product yield of 55%, but with a rapid deactivation giving < 22% yield of HDO products after 25 h on stream.

Catalyst deactivation is believed to be caused by carbon deposition (3.5-9.5 wt% on spent catalysts) and exchange of S by O at the active MoS_2 edges. S-O exchanges may be mitigated with a higher H_2S concentration. In fact, a higher H_2S concentration reactivated and stabilized the catalyst and improved the

HDO/cracking selectivity in experiments with EG WHSV = 19 h^{-1}, see Figure 1. DFT calculations have however indicated that a too high concentration of H_2S inhibits S-vacancy formation at the MoS_2 S-edge thereby potentially limiting HDO. In-situ Quick-EXAFS has thus been applied to study the effect of varying H_2O/H_2S ratios on catalyst composition. The magnitude of the Fourier Transformed in-situ EXAFS spectra (Figure 2A) shows the transition from oxide (MoO_x) to sulfide (MoS_2) during catalyst sulfidation. The EXAFS fit for the resulting sulfide phase shows contributions from Mo-S (2.40Å) with Coordination Number (CN) = 4.2±0.3 and Mo-Mo (3.15Å) with CN = 0.37±0.07. The presence of a small Mo-O contribution (Mo-O (1.61Å), CN = 0.24±0.07) together with the low Mo-S CN could indicate incomplete sulfidation and is possibly caused by interaction between the small and highly dispersed MoS_2 crystallites and the support. The morphology was validated with High-Angle Annular Dark-Field Scanning TEM (HAADF-STEM), see Figure 3B.

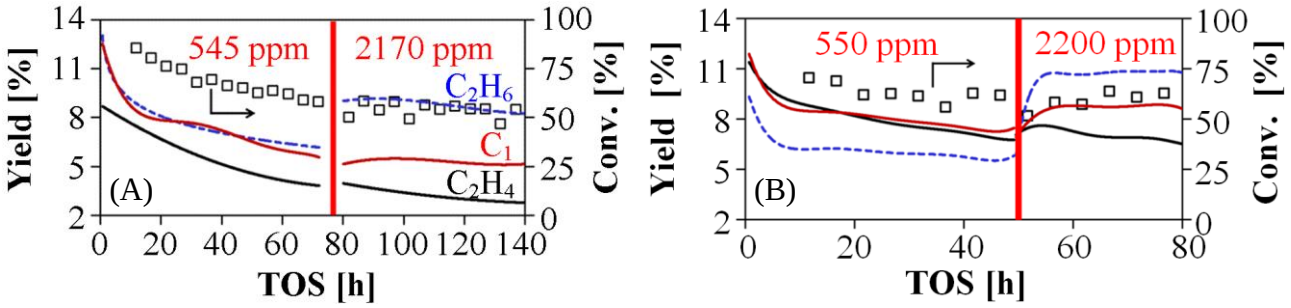

Figure 1. Time on stream (TOS) profiles for EG conversion (□) and gas product yields (**ethane**, **ethylene** and **C_1**) for Ni-$MoS_2/MgAl_2O_4$ (A) and Co-$MoS_2/MgAl_2O_4$ (B) at 400°C, EG WHSV = 19 h^{-1}, 28 bar H_2, 545-2200 ppm H_2S (noted with red text) and total pressure 40 barg.

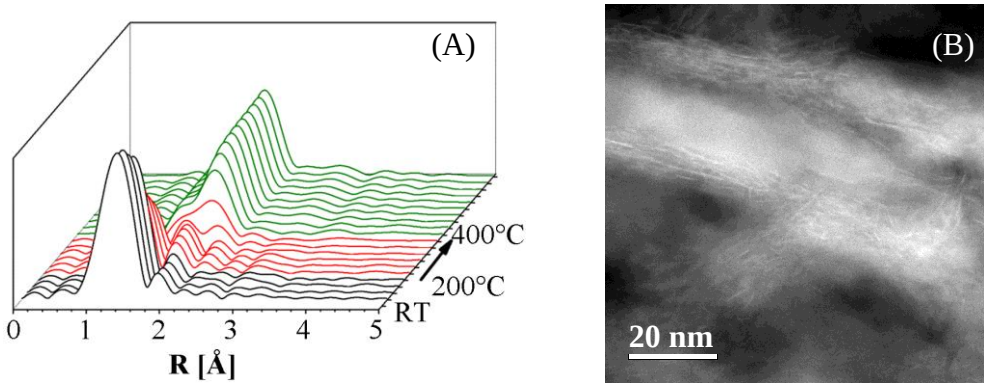

Figure 2. A) Magnitude of the Fourier Transformed in-situ EXAFS spectra (Mo-K-edge) for in-situ sulfidation of $MoS_2/MgAl_2O_4$ going from oxide (MoO_x, black), through transition phases (red) to a sulfide (MoS_2, green). B) HAADF-STEM image of Co-$MoS_2/MgAl_2O_4$. Co-MoS_2 crystallites are visible as bright slabs.

DFT calculations indicate that promotion with Ni compared to Co results in more adsorbed H atoms at the S-edge of MoS_2. This higher hydrogen availability could explain the higher yield of ethane compared to ethylene observed for Ni-$MoS_2/MgAl_2O_4$ (Figure 1A). DFT calculations for EG HDO reaction pathways are being conducted. Future experiments will be performed with mixtures of ethylene glycol and other oxygenates such as acetic acid and phenol to study e.g. inhibition by competitive adsorption.

3. Conclusions

To our knowledge, this is the first catalytic HDO study which combines the experimental and theoretical investigation with advanced in-situ EXAFS characterization to unravel the influence of promotion and H_2O/H_2S on catalytic HDO over MoS_2 catalysts. Understanding the mechanisms behind this influence is a key step in optimizing the catalytic hydropyrolysis process.

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